Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Chromatography A, 1030 (2004) 109–115
JOURNAL OF CHROMATOGRAPHY A
www.elsevier.com/locate/chroma

Potential of coacervation processes for the extraction of amphiphiles (linear alkyl benzenesulphonates) from sewage sludge samples prior to liquid chromatography

Francisco Javier Ruiz, Soledad Rubio, Dolores Pérez-Bendito*

Department of Analytical Chemistry, Facultad de Ciencias, Edificio Anexo Marie Curie, Campus de Rabanales, 14071 Cordoba, Spain

Abstract

A new approach was developed for the monitoring of linear alkyl (C_{10}–C_{13}) benzenesulphonates (LASs) in sewage sludge. It was based on their extraction with the anionic surfactant sodium dodecanesulphonate (SDoS) that undergoes coacervation under acid conditions. The target compounds formed mixed aggregates with SDoS by ideal hydrophobic interactions which made possible the breakdown of LAS–sludge interactions and provided high extraction yields. Variables affecting extraction were optimised using a fortified dehydrated sludge. Recoveries for LASs were found independent on the length of alkyl chain. Liquid chromatography–fluorimetry was used for separation and detection of LAS homologues. Detection limit for LAS in the sludge was 5 mg/kg. Concentration levels of total LASs in activated and dehydrated sludge collected from two different sewage treatment plants were in the range 0.26–0.56 g/kg with LAS homologues ranging from 29 to 223 mg/kg. The method did not require clean-up or preconcentration steps.

Keywords: Sewage sludge; Environmental analysis; Coacervation; Surfactants; Alkyl benzenesulphonates, linear; Sodium dodecanesulphonate

1. Introduction

Aqueous solutions of ionic surfactants, proteins, synthetic polymers and some microemulsions can undergo separation of a low volume surfactant–rich phase from the aqueous bulk induced by proper conditions [1–3]. Examples are changing parameters such as the pH, or adding a second substance such as a concentrated aqueous ionic salt solution or an organic solvent. Also, it can be induced in systems having two dispersed hydrophilic colloids of opposite electric charges. This phenomenon, termed coacervation, has been scarcely exploited for analytical purposes [4–6] in spite of coacervation can greatly extend the scope of micelle-mediated phase separations.

Ionic surfactants have a high potential for the extraction of amphiphiles on the basis of the formation of analyte–extractant mixed aggregates by hydrophobic, electrostatic and specific interactions [7–9]. Hydrophobic interactions lead to the formation of randomly mixed amphiphiles aggregates which is considered as the ideal component of mixing. Electrostatic interactions provide the basis for the non-ideal component of mixing in the aggregate and become progressively stronger is going from mixtures of the same amphiphile type to those of opposite charge. Specific interactions (i.e. between quaternary ammonium groups and aromatic rings [10]) can also reinforce the formation of mixed aggregates.

In a previous research, the ability of the acid-induced coacervation of sodium dodecanesulphonate to extract cationic surfactants from sewage sludge has been proved [11]. Ideal hydrophobic and non-ideal electrostatic interactions between the extractant and the target compounds led to the formation of mixed aggregates that facilitated the breakdown of sludge–cationic interactions and provided high extraction yields. The proposed method was found quantitative, fast and simple. Because of these results, it is interesting, both from a theoretical and practical point of view to go deeply into the ability of coacervative extractions to extract amphiphiles of different nature from solid samples.

Lots of amphiphiles are of concern in different areas such as biomedical, pharmacy and the environment. In the environment, amphiphiles include surfactants, many pesticides, phthalates etc. When they are discharged into wastewater

* Corresponding author. Tel.: +34-957-218644; fax: +34-957-218644.
E-mail address: qa1pebem@uco.es (D. Pérez-Bendito).

0021-9673/$ – see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/j.chroma.2003.11.064

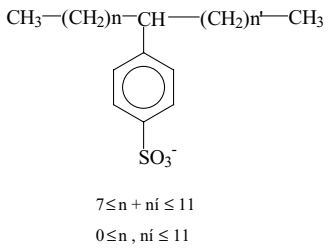

Fig. 1. General chemical structure of the linear alkyl benzenesulphonates.

treatment plants (WWTPs) or reach natural waters, a significant proportion, that depends on their nature, becomes associated to the particulate fraction (i.e. sewage sludge, sediment, etc.). Amphiphiles extractions from solid environmental samples have been based on their solubilisation in organic solvents, in which their hydrophobic character has been mainly exploited. Soxhlet based repetitive extractions using high volumes of organic solvents, with extraction yields depending on the alkyl chain length of the target compounds are commonly used.

This article deals with the potential of the acid-induced coacervation of sodium dodecanesulphonate [6] to extract amphiphiles from solid environmental samples based exclusively on ideal hydrophobic interactions. The aim was to compare the ability of coacervative- and organic solvent-based extractions when the same effect (i.e. hydrophobic) was used to solubilisation of the target compounds. For this purpose, the anionic surfactants linear alkyl benzenesulphonates (LASs), that are the major surfactant used on the market were selected. Both, analytes and extractant (sodium dodecanesulphonate, SDoS) bear the same polar group and therefore only hydrophobic interactions will be the leading force to the formation of LAS–SDoS aggregates. On the other hand, LAS commercial samples are a mixture of C_{10}–C_{13} homologues (Fig. 1) so, the influence of the alkyl chain length on the efficiency of coacervative extraction can be assessed. Sewage sludge was the matrix selected for this study because the organic matter in domestic wastewaters, mainly made up of carbohydrates, fats and proteins [12], exerts a strong attraction for amphiphiles. The influence of the different parameters affecting both extractive efficiency and preconcentration factors was assessed. Matrix effects were widely investigated. The feasibility of the method developed was illustrated by the analysis of LAS homologues in activated and dehydrated sludge from two WWTPs.

2. Experimental

2.1. Apparatus

The liquid chromatographic system used (Spectra System SCM1000, ThermoQuest, San Jose, CA, USA) consisted of a P4000 quaternary pump, a UV6000LP diode-array detector and a FL3000 fluorescence detector. In all experiments, a Rheodyne 7125NS injection valve, with a 20 μl sample loop was used (ThermoQuest). The inner surface of the valve was coated with Teflon in order to prevent the possible corrosion caused by the acidity of the sample. The stationary-phase column was a 25 cm Nova-Pak C_{18} column, with 4.6 mm i.d., from Waters (Milford, MA, USA). For sample preparation, a Telstar Cryodos-50 freeze-dryer was employed.

2.2. Chemicals

All reagents were of analytical reagent-grade and were used as supplied. SDoS was obtained from Fluka (Madrid, Spain). Hydrochloric acid, HPLC-grade acetonitrile and methanol were obtained from Panreac (Sevilla, Spain). Analytical grade sodium perchlorate was purchased from Merck (Darmstadt, Germany). Petrelab P-550, a C_{10}–C_{13} commercial LAS product, was kindly supplied by Masso and Carol (Barcelona). The proportional composition of the different homologues was as follows: C_{10}, 9.3%; C_{11}, 37.6%; C_{12}, 35.2%; C_{13}, 17.9%. Standard solutions of LASs were prepared in distilled water. Ultra-high-quality water was obtained from a Milli-Q water purification system (Millipore, Madrid, Spain).

2.3. Samples

Activated and dehydrated sludge samples were collected in plastic containers from two WWTPs (Pozoblanco and Baena) in the south of Spain, in December 2002 and March 2003, respectively. Pozoblanco WWTP receives domestic effluents and Baena WWTP receives about 30% of industrial effluents (mainly from laundries and olive oil industries) mixed with about 70% domestic wastewaters. Dehydrated sludge samples were freeze-dried, finely ground (<0.5 mm), and stored in amber bottles at 4 °C until analysis. Activated sludge samples were previously filtered, and then processed as dehydrated sludge.

Spiked samples were prepared from dehydrated sludge collected in the Pozoblanco WWTP (May 2002). Samples were freeze-dried and finely ground. Then, 10 ml of 300 mg/l LAS aqueous solution were added to 25 g (dry mass) of sludge. Samples were allowed to interact with the natural organic matter for 1 day under nitrogen to prevent aerobic degradation and under stirring. Then, the sludge was freeze-dried, ground and stored in amber bottles at 4 °C.

2.4. LAS coacervative extraction

The steps followed for extraction of LASs from sewage sludge were as follows: the sample (0.1 g) was mixed with 10 ml of 0.1 M HCl and stirred at 73 rad/s for 5 min. The acid solution containing alkaline and alkaline-earth metals was separated by centrifugation and discarded. Then, 10 ml of 3% SDoS in 4 M HCl was added to the solid sample and the mixture stirred at 73 rad/s (Agimatic-N, Selecta, Barcelona,

Spain) and 40 °C for 40 min. Afterwards, it was centrifuged at 420 rad/s for 10 min. Three phases were observed in the centrifuge tube; the non-dissolved solid matrix at the bottom, a little volume of surfactant-rich phase containing the LASs at the top and aqueous phase between both, containing the surfactant at a concentration near the critical micellar concentration. In order to make easier the separation of the surfactant-rich phase, the temperature was lowered to 0 °C, then this phase, turned gelatinous, dense enough to be separated from the liquid phase using a simple tool (a spatula). Under room temperature, the gelatinous phase rendered liquid (about 1.7) and it was diluted to 5 ml with methanol in a standard flask. Eight sludge samples were treated simultaneously. Before injecting an aliquot in the chromatographic system, the sample was filtered thorough a 0.45 μm nylon membrane filter (0.8 mm × 19 mm, Becton, Dickinson and Company, GA, USA).

2.5. Liquid chromatography–fluorimetry

Acetonitrile–water (70:30, solvent A) and water (solvent B) both containing 0.15 M $NaClO_4$ were used as eluent solvents, at a flow rate of 1 ml/min. The gradient elution program was linear from 33 to 10% B in 22 min and then isocratic for 3 min. The column effluent was monitored at 225 nm of exciting wavelength and 295 nm of emission wavelength.

Calibration curves were obtained by adding 1 ml of aqueous solution containing between 5 μg and 0.2 mg of LASs to 0.1 g of sludge previously treated with 10 ml of 0.1 M HCl to remove alkaline and alkaline-earth metal. After addition of LASs the slurry was stirred at 700 rpm for 10 min and subjected to the coacervative extraction. Correlation between peak areas and LAS homologues concentrations (20–800 ng absolute amount) were determined by linear regression and were typically $r = 0.996$.

3. Results and discussion

3.1. Chromatographic separation of LAS homologues

LASs on the European market is a mixture of closely related isomers and homologues each containing a linear alkyl chain, a benzene ring randomly distributed in all positional isomers except 1-phenyl and a sulphonate group in *para*-position. The linear alkyl chain has typically 10–13 carbon units. Homologues separation of LASs is important in industrial and environmental samples, because detergency, biological degradation and aquatic toxicity depend on the alkyl chain length. Thus, biodegradation and bioconcentration is higher for the longer-chain-length LASs [13–16]. On the other hand, individual analysis of LAS homologues is important to assess the efficiency of the SDoS coacervative extraction as a function of the length of the alkyl chain.

Separation of LAS homologues using reversed-phase LC–UV has generally involved the use of an electrolyte, such as $NaClO_4$, in the mobile phase [17–19]. We tested different gradient elution programs with various combinations of acetonitrile and water, and $NaClO_4$ at several concentrations, with two aims, namely, to obtain homologues resolution at the minimal analysis time and to achieve selectivity from extracted matrix components. Fig. 2 shows two typical chromatograms obtained at experimental conditions under which sludge matrix components and C_{10}-LAS coeluted (Fig. 1(b)) and separation was achieved (Fig. 1(a)), respectively. Non-isocratic conditions were necessary to obtain selectivity. The surfactant SDoS did not interfere in the chromatographic analysis under any of the gradient elution programs tested.

3.2. SDoS coacervative extraction of LASs from sewage sludge

A significant proportion of LASs in raw sewage (10–35%) adsorbs to particulate matter [20]. The process of adsorption is primarily driven by the hydrophobic effect and specific or electrostatic interactions [21]. The extent of adsorption depends on a number of factors [22], the length of the alkyl chain being significant. It has been stated [23] that for each carbon atom added to the alkyl chain a two- to three-fold increase in the K_s (association constant) for LASs occurs. Other factors influencing the LAS amount present in sewage sludge are the presence of metal ions [20] (particularly Ca^{2+} that precipitates LASs), and the type of treatment the sludge undergoes [24] (aerobically treated sludge typically contain LAS concentrations in the range 100–500 mg/kg dry mass, whereas anaerobically treated sludge have LAS concentrations between 5000 and 15 000 mg/kg dry mass).

Extraction of LASs from sewage sludge is commonly performed using Soxhlet or sonication with basic methanol [20,25–28]. Typical experimental conditions include two to three repetitive extractions, high volumes of organic solvents and long extraction times (about 4 hs). Therefore, more rapid and simple extraction method should be developed for analysis of LASs in sewage sludge.

3.2.1. Behaviour of LASs under SDoS coacervative extraction conditions

According to the phase diagram of SDoS in hydrochloric acid aqueous solutions [29], two coexisting isotropic phases exist for this surfactant in the range 2.5–5 M HCl. Alkyl benzenesulphonates also undergo coacervation, although at considerable higher acid conditions (between about 5 and 9 M HCl) [6]. Below 5 M HCl, LASs precipitate as alkyl benzenesulphonic acids. We checked that precipitation was not quantitative between 10^{-4} and 5 M HCl for LAS concentrations ranging from 1 to 500 mg/l. At the LAS concentrations of interest for calibration (about 1–40 mg/l) and 4 M HCl, the percentage of precipitation for LASs was found to be about 20–25%. Partitioning of LAS homologues to the

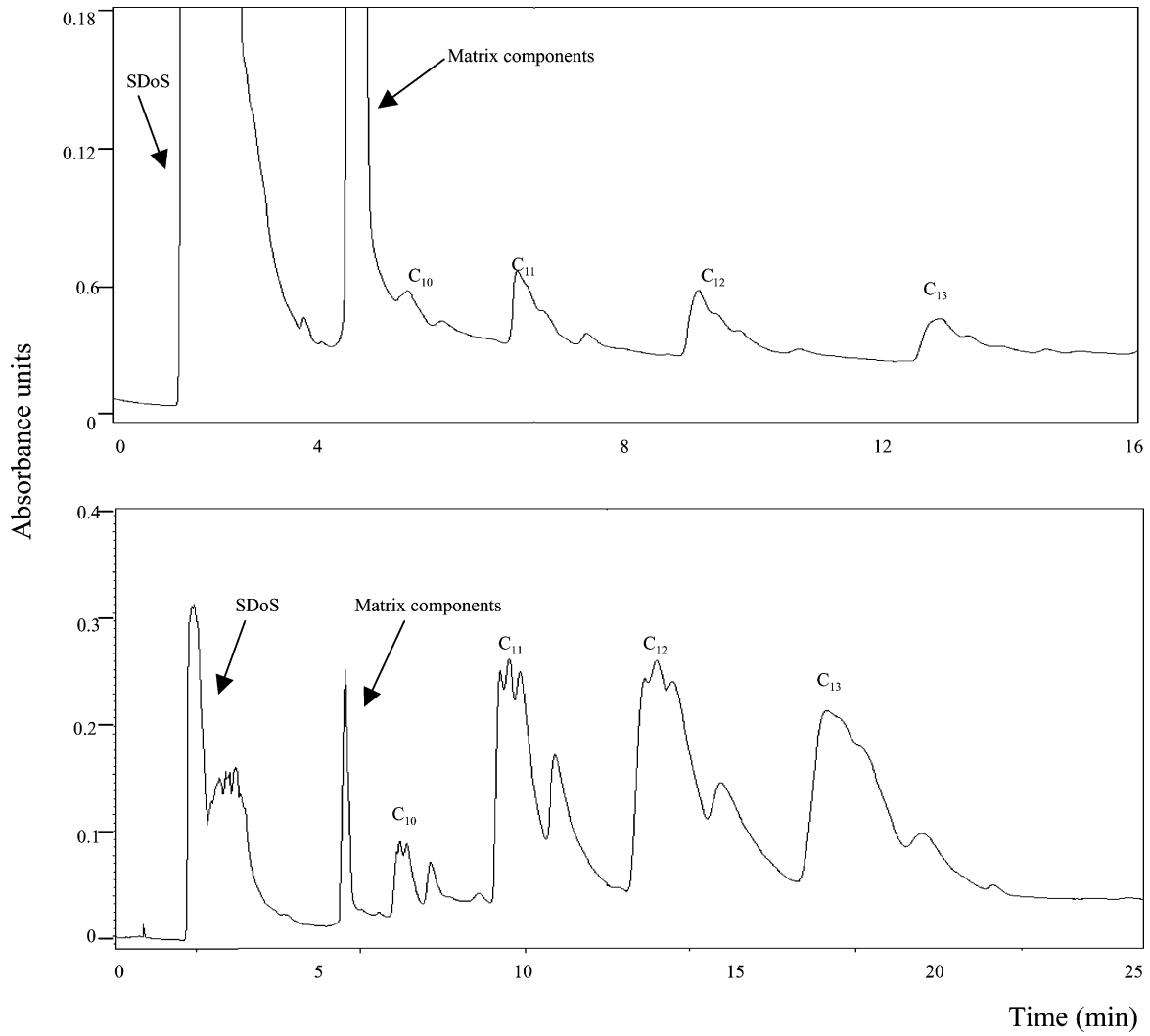

Fig. 2. LC–fluorimetry chromatograms obtained from a fortified sludge sample collected in the WWTP of Pozoblanco (0.1 g). Mobile phase: acetonitrile–water (70:30, solvent A) and water (solvent B) both containing 0.15 M $NaClO_4$. Flow rate: 1 ml/min. Stationary-phase column: 25 cm Nova-Pak C_{18} (4.6 mm i.d., Waters). Gradient elution program: (a) linear from 21 to 13% B in 20 min and then isocratic for 5 min; (b) as specified in Section 2. LAS amount injected: (a) 80 ng; (b) 240 ng.

SDoS surfactant-rich phase from the water phase was found to be about 75–80% under a variety of experimental conditions (equilibration time, 5–80 min; temperature, 20–60 °C; [HCl] = 2.5–4 M; [SDoS] = 1–3%) which indicated that SDoS did not affected the precipitation equilibrium of alkyl benzenesulphonic acids.

It was also checked from preliminary experiments that the matrix components extracted from different sludge had hardly effect on the precipitation of alkyl benzenesulphonic acids. Thus, recoveries obtained from the addition of LAS standards to the SDoS rich phase resulting from the extraction of 0.1 g of no spiked sludge ranged from 76 to 82%.

As earlier specified, LASs are retained in sewage sludge by both adsorption and precipitation with Ca^{2+} (LAS-Ca). Since Ca^{2+} also precipitates the extractant SDoS, we investigated its ability to extract LAS-Ca. For this experiment, we considered extreme conditions, namely, the LAS concentration in sludge was 40 g/kg and all LASs were as LAS-Ca. The highest LAS concentrations in sludge (about 30 g/kg) have been reported for a Spanish region in presence of a very high water hardness (>500 mg/l as $CaCO_3$) [30], however, LASs in aerobic sludge rarely exceeds 0.5 g/kg. Investigations were carried out by precipitating the LAS amount corresponding to 0.1 g of sludge in an aqueous medium with Ca^{2+} concentrations that were, respectively a half, equal and twice the LAS molar concentration. Precipitation of LASs was detected in all experiments. After centrifugation, the supernatant and precipitate were subjected to coacervative extraction with SDoS. Considering the sum of both fractions, LAS recoveries ranging from 76 to 83% were obtained (the rest precipitated as alkyl benzenesulphonic acid), thus confirming the ability of SDoS to extract LAS-Ca.

Table 1
Mean percent recoveries[a] obtained for the extraction of C_{10}–C_{13} LAS homologues from sewage sludge (0.1 g) as a function of SDoS concentration

SDoS (%)	C_{10}	C_{11}	C_{12}	C_{13}	Recovery (%)[b]
1.5	52	48	46	46	48
2	75	72	71	70	72
2.5	77	74	70	71	73
3	99	99	98	98	98
4	90	90	88	85	87

[a] Based on three replicates; range of R.S.D. values 1–5%.
[b] Average recoveries of LAS homologues. Experimental conditions: 40 °C, 4 M HCl and 1 h.

3.2.2. Optimisation of the extraction process

As no standard reference materials were available, spiked dehydrated sludge was used to optimise the parameters potentially influencing the extraction efficiency of LASs, namely, surfactant amount, temperature, HCl concentration, matrix components, extraction time, etc. The effect of these parameters on the surfactant-rich phase volume and therefore on the preconcentration factor achieved was also investigated. Three replicates were made to get a mean value. Recoveries were calculated from calibrations carried out with aqueous LAS standards, therefore extraction was considered quantitative when recoveries were about 75–80%, considering the simultaneous precipitation of alkyl benzenesulphonic acids under the acid conditions used.

Before extraction, removal of the alkaline-earth metals present in sludge as carbonates was necessary since they yield insoluble salts with SDoS. Stirring of the sample with 0.1 M HCl for 5 min was enough to remove the alkaline-earth metals without losses of LASs in the acid phase discarded.

Table 1 shows some of the recoveries obtained for LAS homologues as a function of SDoD concentration. The recoveries calculated for total LASs are also included. The extraction efficiency was found to be practically independent on the length of the alkyl chain. The phase volume ratio (volume of surfactant-rich phase/volume of aqueous solution, after the extraction step) was linearly dependent on the percentage of SDoS used as extractant, thus influencing the volume of the extracts obtained and as a result the detection limits that can be achieved. Accordingly, a compromise should be always achieved between recovery and preconcentration. The precision obtained decreased at SDoS concentrations above 4% probably due to the greater difficult in manipulating the high volumes obtained for the surfactant-rich phase. A percentage of 3% SDoS which gave to about 1.7 ml of surfactant-rich phase is recommended.

The influence of the temperature on the efficiency of SDoS to extract LAS from sludge was studied in the range 20–70 °C (results not shown). The percentage of extraction increased about 5% when the temperature ranged from 20 to 40 °C. No significant increments were observed for larger temperature values. Therefore, it is recommended that extractions are carried out at 40 °C.

The kinetics of extraction of LASs from the aqueous phase to SDoS micelles is very rapid and as a result the partition equilibrium is achieved in about 2 min. In solid samples, the kinetics of partition between the solid and the micellar phase will be mainly governed by the kind and site of binding of analytes to the porous matrix. In order to investigate the influence of the time of extraction on the ability of SDoS to extract LASs from the sludge sample, this variable was tested in the ranged between 10 min and 1 h (times below 10 min produced low precision recovery measurements). Recoveries for LASs increased from about 73 to 82% in the 10–40 min interval and then kept constant. They were independent on the length of the alkyl chain. An extraction time of about 40 min is recommended.

Acid conditions (2.5–5 M HCl) are necessary to get the separation of SDoS in two isotropic phases in an aqueous medium. Organic components are known to influence surfactant phases separation diagrams [1,2] and therefore sludge matrix components could affect SDoS coacervation. For this reason, we studied the influence of hydrochloric acid concentration on the efficiency of SDoS to extract LASs from sludge (0.1 g) in a wide interval (1–8 M). It was found that coacervation of SDoS occurred in the range 2.5–4.3 M hydrochloric acid, therefore the superior limit was reduced with respect to an aqueous medium. In this interval, extraction efficiencies for LASs were about 82% from 3.5 M HCl and the volume of the surfactant-rich phase decreased from 3 to 1.7 ml. A HCl concentration of 4 M is recommended for extraction of the spiked dehydrated sludge used for optimisation purposes in order to achieve maximal extraction efficiency and preconcentration.

As sludge matrix components influenced the SDoS phases separation diagram, the effect of different amounts of sludge (0.1–1 g) on the coacervation process was investigated. For this purpose, HCl and SDoS concentrations ranging from 1 to 8 M and 1 to 10% were tested. It was found that the amount of sludge greatly influenced the rich phase volume obtained (Table 2), however, the HCl concentration interval in which coacervation occurred hardly was modified. As it is logical, the surfactant concentration required for extraction increased in proportion to the amount of sludge increased. The minimum sludge (g):surfactant (%) ratio to get coacervation was about 1:7. So, under the conditions specified

Table 2
Effect of the amount of sludge used for extraction on the SDoS rich phase volume obtained

Sludge amount (g)	ACPE conditions		Surfactant-rich phase volume (ml)
	[HCl] (M)	[SDoS] (%)	
0.05	3	4	5.8
0.1	3	4	4.2
0.2	3	4	3
0.3	3	4	2.2
0.4	3	4	1.2
0.5	3	4	0.5

Table 3
Calibration data obtained by addition of LAS standard to different sludge samples.

Sludge sample	Slope ± S.D. ($\times 10^4$ ng^{-1})	Intercept ± S.D. ($\times 10^6$)	$S_{y/x}$ ($\times 10^6$)	r
Activated (Pozoblanco)	0.16 ± 0.01	−0.09 ± 0.21	0.20	0.997
Dehydrated (Pozoblanco)	0.20 ± 0.02	1.93 ± 0.54	1.28	0.997
Activated (Baena)	0.18 ± 0.02	1.36 ± 0.40	0.90	0.997
Dehydrated (Baena)	0.21 ± 0.02	2.15 ± 0.85	1.30	0.996

in Table 2 (4% SDoS), no coacervation was get for sludge amounts equal or above to 0.6 g. The sample size did not affect to the extraction efficiency for the two different sludge amounts analysed (0.1 and 0.2 g). Therefore, 0.1 g of sludge is recommended for analysis.

3.3. Calibration data

Because the complexity of sludge samples, the low selectivity of UV detection and the possibility that matrix components of some sludges could affect precipitation of alkyl benzenesulphonic acids, calibration curves were constructed by applying the complete procedure to 0.1 g of sewage sludge fortified with a solution containing LASs, previous removal of alkaline and alkaline-earth metals by 0.1 M HCl. Table 3 shows the results obtained for calibrations from four fortified (5 μg–0.2 mg) sludge samples, expressed as total concentration of LASs. Identical responses were obtained for the different homologues. The curves obtained were linear in the range studied, from 20 to 800 ng (absolute amount injected), and the correlation coefficients were about 0.996 thus indicating good performance of the methodology developed. Similar slopes were found from sludge samples of different composition, so a single calibration could be used for analysis of different sludges.

The instrumental detection limits were calculated using a signal-to-noise ratio of 3. It was about 2 ng. Taking into account the amount of sample extracted and the volume of extract injected, the detection limit of LAS in sludge samples was calculated to be 5 mg/kg. Thus, the method developed has the capability of detecting low concentrations of LASs in environmental sludge samples.

The precision of the method was evaluated by extracting eleven independent fortified sludge samples. The relative standard deviation ranged between 10 and 15% for the different homologues, which indicated a good reproducibility of the approach developed in this work.

The possible interference of non-ionic surfactants was carefully investigated since they are components of sludge samples and they can be easily extracted by SDoS because of their amphiphile nature. Sludge concentrations expected for alkylphenol ethoxylates are higher in anaerobically digested sludge (900–1100 mg/kg [31]) than in aerobically digested sludge (0.3 mg/kg [32]), and considerably lower that LAS concentrations [24]. Non-ionic surfactants selected for this study were nonylphenol ethoxylate and octylphenol ethoxylate which were added to 0.1 g of LASs at equimolecular and 10-fold the LAS concentration. No interference was detected in the extraction efficiency of LASs. No coelution occurred under the elution program used.

3.4. Sewage sludge samples

The performance of the method was evaluated by analysing activated and dehydrated sewage sludge from two WWTPs located in the south of Spain (Pozoblanco and Baena). They were selected on the basis that they receive domestic and domestic/industrial influents, respectively. Both of them apply biological treatment. Volumes of surfactant-rich phase between 1.4 and 1.7 ml were obtained for all samples analysed using the concentration of HCl recommended (4 M), except for the activated sludge from Baena. For this sample, coacervation occurred at lower HCl concentrations. Adequate volumes of surfactant-rich phase (1.4–1.6 ml) were obtained from 3 M hydrochloric acid concentration. The acid concentration selected for its analysis was 3.5 M.

Table 4 shows the concentrations found for the different LAS homologues, expressed as the mean value (n = 3) and the corresponding standard deviation. The LAS homologue distribution in sludge from Pozoblanco was similar to that of commercial products, for which the mole ratio C_{10}:C_{11}:C_{12}:C_{13} is typically 13:30:33:24. However, the sludge from Baena showed a distribution similar to that found by other authors (C_{10}:C_{11}:C_{12}:C_{13} mole ratio = 7:24:40:29) [13,30,33] which is a consequence of the preferential adsorption of higher homologues. This different distribution could be related with the particular form in which LASs are retained in the sludge (precipitated with metals or adsorbed), although more data are necessary to confirm this assumption. Total LAS concentration was lower than

Table 4
Mean concentration[a] (mg/kg) ± S.D. of C_{10}–C_{13} LAS homologues found in sewage sludges collected from two wastewater treatment plants (WWTPs), analysed by the SDoS coacervative extraction approach.

LAS homologue	Sludge from Pozoblanco		Sludge from Baena	
	Activated	Dehydrated	Activated	Dehydrated
C_{10}	54 ± 6	35 ± 5	36 ± 3	29 ± 2
C_{11}	115 ± 10	83 ± 12	139 ± 8	102 ± 8
C_{12}	108 ± 9	84 ± 11	223 ± 13	177 ± 12
C_{13}	75 ± 7	61 ± 8	160 ± 12	136 ± 10

[a] Based on three replicates.

0.5 g/kg for the analysed samples, except for the activated sludge from Baena. All homologues underwent biodegradation in the WWTPs; differences in LAS concentration between activated and dehydrated sludge were about 20–25%.

4. Conclusions

Some conclusions can be inferred from the results obtained in this study that are of interest for the monitoring of amphiphiles in environmental solid samples. Thus, coacervative extraction based on the formation of mixed aggregates between the extractant and analytes by hydrophobic interactions has a strong capability to break sludge–LAS bonds, originating high extraction yields. The results obtained from the optimisation of the extraction process are basically similar to those previously found [11] and they seems to be of general character for the extraction of compounds from solid samples [34]. Briefly, the concentration of the surfactant used as extractant is of primary importance to maximise recovery, and the volume of the surfactant-rich phase obtained depends on extractant/HCl concentration and the organic nature of matrix components. So, it is important to make it to a fixed volume.

The main advantages of the method developed here for the monitoring of LASs in sewage sludge are as follows. The extraction of C_{10}–C_{13} homologues is carried out in an aqueous medium using an extraction time of 40 min and mild conditions (40 °C). No special equipment is required which makes possible to perform simultaneous treatments. Also, extractions are not dependent on the length of the alkyl chain of LASs. These characteristics compare favourably with those of the classical extraction of LASs from solid samples with basic methanol, where two to three repetitive extractions with high volumes of organic solvents and sample treatments of 3–4 h using Soxhlet are required [25–28]. So, hydrophobic interactions between amphiphiles leading to the formation of mixed aggregates seems to have higher extraction capability that solubilisation of amphiphiles in organic solvents.

Acknowledgements

The authors gratefully acknowledge financial support from the Spanish CICyT (project BQU 2002-01017). They also thank the Pozoblanco and Baena WWTP personnel for kindly collecting the sludge samples.

References

[1] W.L. Hinze, D.W. Armstrong (Eds.), Ordered Media in Chemical Separations (ACS Symposium Series No. 342), American Chemical Society, Washington, DC, 1987.
[2] W.L. Hinze, E. Pramauro, Crit. Rev. Anal. Chem. 24 (1993) 133.
[3] E. Pramauro, E. Pelizzetti, Surfactants in Analytical Chemistry–Applications of Organized Amphiphilic Media, Elsevier, New York, 1996.
[4] X. Jin, M. Zhu, E.D. Conte, Anal. Chem. 71 (1999) 514.
[5] S. Igarashi, T. Yotsuyanagi, Microchim. Acta 106 (1992) 37.
[6] I. Casero, D. Sicilia, S. Rubio, D. Pérez-Bendito, Anal. Chem. 71 (1999) 4519.
[7] J.F. Scamehorn, in: J.F. Scamehorn (Ed.), Phenomena in Mixed Surfactant Systems (ACS Symposium Series No. 311), American Chemical Society, Washington, DC, 1986, p. 1.
[8] M.J. Rosen in: J.F. Scamehorn (Ed.), Phenomena in Mixed Surfactant Systems (ACS Symposium Series No. 311), American Chemical Society, Washington, DC, 1986, p. 144.
[9] P.M. Holland, D.N. Rubingh, in: D.N. Rubingh, P.M. Holland (Eds.), Cationic Surfactants: Physical Chemistry (Surfactant Science Series, vol. 37), Marcel Dekker, New York, 1990, p. 141.
[10] M. Grätzel, K. Kalyanasundaram (Eds.), Kinetics and Catalysis in Microheterogeneous Systems, Marcel Dekker, New York, 1991.
[11] F. Merino, S. Rubio, D. Pérez-Bendito, J. Chromatogr. A 998 (2003) 143.
[12] M. Henze, P. Harremoes, E. Arvin, J.C. Jansen, Wastewater Treatment–Biological and Chemical Processes, Springer, Berlin, 1997.
[13] A. DiCorcia, R. Samperi, A. Belloni, A. Marcomini, M. Zanette, K. Lemr, et al., Riv. It. Sostanze Grasse 71 (1994) 467.
[14] P. Eichhom, M.E. Flavier, M.L. Paje, T.P. Knepper, Sci. Total Environ. 269 (2001) 75.
[15] J. Tolls, Thesis, Utrecht University, 1998, ISBN No. 90-393-1676-1.
[16] L. Sarrazin, Y. Limouzin-Maire, P. Rebouillon, Toxicol. Environ. Chem. 69 (1999) 487.
[17] K. Inaba, K. Amano, Int. J. Environ. Anal. Chem. 34 (1988) 203.
[18] A. Nakae, K. Tsuji, M. Yamanaka, Anal. Chem. 53 (1981) 1818.
[19] A. DiCorcia, F. Casassa, C. Crescenzi, A. Marcomini, R. Samperi, Environ. Sci. Technol. 33 (1999) 4112.
[20] J.L. Berna, A. Moreno, J. Ferrer, Chem. Technol. Biotechnol. 50 (1991) 387.
[21] J.C. Westall, H. Chen, W.J. Zhang, B.J. Brownawell, Environ. Sci. Technol. 33 (1999) 3110.
[22] D. Prats, F. Ruiz, B. Vazquez, D. Zarzo, J.L. Berna, A. Moreno, Environ. Toxicol. Chem. 12 (1993) 1599.
[23] H.A. Painter, Environ. Chem. 3 (1992) 2.
[24] J. Jensen, Sci. Total Environ. 226 (1999) 93.
[25] L. Comellas, J.L. Portillo, M.T. Vaquero, J. Chromatogr. A 657 (1993) 25.
[26] D. Prats, F. Ruiz, B. Vázquez, D. Zarso, Jom. Com. Deterg. 22 (1991) 479.
[27] W. Giger, A.C. Alder, P.H. Brunner, A. Marcomini, H. Siegrist, Tenside Deterg. 26 (1989) 95.
[28] A. Marcomini, W. Giger, Tenside Deterg. 25 (1988) 4.
[29] D. Sicilia, S. Rubio, D. Pérez-Bendito, Anal. Chim. Acta 460 (2002) 13.
[30] J.L. Berna, J. Ferrer, A. Moreno, D. Prats, F. Ruiz Bevia, Tenside Surf. Deterg. 26 (1989) 101.
[31] A. Marcomini, P.D. Capel, T.H. Lichtensteiger, P.H. Brunner, W. Giger, J. Environ. Qual. 18 (1989) 523.
[32] J. Torslov, L. Samsoe-Peterson, J.O. Rasmussen, P. Kristensen, Use of Wastewater Products in Agriculture–Contamination Level, Environmental Risk Assessment and Recommendations for Quality Criteria, VKI Report No. 366, 1997.
[33] L. Cavalli, A. Gellera, A. Landone, Environ. Toxicol. Chem. 12 (1993) 1777.
[34] F. Merino, S. Rubio, D. Pérez-Bendito, J. Chromatogr. A 962 (2002) 1.